Australian Government Initiative

WATER QUALITY
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National Acid Sulfate Soils Guidance

National acid sulfate soils sampling and identification methods manual

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Water Quality Australia is an Australian Government initiative in partnership with state and territory governments.

Appendix A: Soil field tests

This Appendix provides information on how to perform field pH and carbonate tests and interpret their results. It is important to note that, while a useful exploratory tool, field tests are indicative only. They cannot be used as a substitute for laboratory analysis to determine the presence or absence of acid sulfate soils (ASS).

Further laboratory analysis is also needed to quantify the acidity and other hazards.

Details on the laboratory analyses required for ASS are provided in the National Acid Sulfate Soils Identification and Laboratory Methods Manual (Sullivan et al. 2018b).

A1.1 Soil field test equipment

It is important that prior to conducting the field tests, the appropriate testing equipment is obtained. For a basic set up the following items are required:

1) pH meter and electrode (charged and calibrated),
2) at least 2 buffer solutions (for example pH 4.0 and pH 7.0),
3) centrifuge tubes or beakers – wide, unbreakable, heat resistant and clear (for example Falcon 50 mL polypropylene),
4) centrifuge tube or jar rack marked with soil sample depths – use a separate rack for pH_F tests and pH_{FOX} tests in case they bubble over,
5) stirrers for centrifuge tubes,
6) 30% hydrogen peroxide (H_2O_2) pH adjusted to 4.5–5.5,
7) storage bottle for H_2O_2,
8) sodium hydroxide (NaOH) to raise pH of peroxide to 4.5–5.5 (pH 5.5 ideal),
9) deionised (DI) water,
10) squirt bottle for DI water,
11) tissues,
12) gloves and safety glasses,
13) protective clothing,
14) bucket to collect used soil and hydrogen peroxide,
15) bucket and brush to clean tubes for next sample,
16) recording sheets,
17) excess water for rinsing,
18) first aid kit – especially eye wash solutions, and
19) 1 M hydrochloric (HCl) acid to test for shell presence.

A1.2 Conducting field tests – some considerations

When the analytical results are reported, both the field test results and informative soil profile descriptions will aid the interpretation of the laboratory results and help provide a better understanding of the soil properties and behaviour on the site, especially with respect to the acidity hazard.

When performing pH_F tests, soil samples must be analysed as soon as possible after sampling. If Reduced Inorganic Sulfur (RIS) are present, they are often capable of rapid oxidation causing substantially lowered pH_F values. Delayed determinations of pH_F may provide results that do not faithfully represent pH conditions in the field at the time of sampling.

The rate of reaction in the pH_{FOX} test is temperature dependent and can take up to an hour to complete under cold conditions. It is important to allow sufficient time for the reaction to occur, especially in cool weather.

Field pH tests should be performed on site, however, there are many areas (for example wetlands) where performing field tests in situ can prove difficult (for example too wet, mosquito problems). In such situations, samples should be preserved (for example kept on dry ice), taken to a suitable location for the conduct of field tests and the delay in time between sampling and ‘field’ analysis recorded with the field test results.

A1.3 On-site chemical and material safety precautions

A1.3.1 Hydrogen peroxide

Care needs to be taken when using hydrogen peroxide (H_2O_2) in the field. Hydrogen peroxide (30%) is used as the primary reagent in the pH_{FOX} test. The concentration is 10 times stronger than the peroxide commonly found in household medicine cabinets. The reaction of peroxide with soil containing RIS may produce sulfurous gases and generate heat in excess of 90 °C.

Caution: 30% hydrogen peroxide is a strong oxidising agent and should be handled carefully with appropriate eye and skin protection. This test is suitable for experienced operators only.

The peroxide when first received may have a pH of 3.5 or lower. Chemical companies commonly put stabilisers in the peroxide to prevent it from decomposing and releasing oxygen by keeping the pH low. The pH required for the pH_{FOX} is pH 4.5–5.5; this may be obtained by adding sodium hydroxide (NaOH; pH14).

Since both of these chemicals are highly corrosive and many of the long-term side effects are not fully known, it is recommended the following precautions are taken when performing field tests.

Always:

- use gloves, safety glasses, lab coat or protective clothes,
- conduct pH peroxide test in a well-ventilated area,
- use test tubes capable of withstanding rapid heat changes and high temperatures,
- avoid skin and eye contact with peroxide, and
- label all peroxide bottles with safety data information.

A1.3.2 Other chemicals

Several other chemicals are used in the field when sampling suspected ASS materials. Buffering solutions and potassium chloride (KCl) solutions are used to calibrate and maintain pH meters and care should be exercised when using these substances. Follow the appropriate safety directions on Safety Data Sheets (SDS).

Hydrochloric acid (HCl) is used when performing tests to assess the presence of carbonates in soil material (see Field carbonate test). Hydrochloric acid is strongly acidic and is very corrosive to the skin, therefore, caution is required when using it. Again, follow the appropriate directions outlined in the SDS.

Store HCl separately from buffer solutions as HCl gas may slowly diffuse through the plastic bottles and alter the buffer solutions.

A1.4 Field pH tests

A1.4.1 Introduction

The pH_F and pH_{FOX} tests have been developed for rapid assessment in the field for the likelihood of ASS. These tests are easy to conduct, quick, and have a minimum set-up cost. The field tests have been developed to give reasonable indication for many soils (provided the tests are performed properly). Although these field tests may provide an indication of ASS presence, they are purely qualitative, indicative, and do not give quantitative measures of the amount of acid that has been or could be produced through the RIS oxidation process.

Field pH tests should be part of any ASS investigation. The field pH tests (both pH_F and pH_{FOX}) should be conducted at 0.25 m intervals on the soil profile, ensuring at least one test per soil layer/horizon.

It is recommended that field tests be conducted on-site. If the tests cannot be performed in the field, tests should be conducted as soon as possible, ensuring appropriate sample and preservation procedures are observed (see the Sample handling, transport and storage section in Section 6 for further details) and delays between sampling and the ‘field’ analysis are recorded with the results.

Samples suspected of containing monosulfides should undergo field pH testing immediately.

The field pH tests outlined below are from the Queensland Acid Sulfate Soils Investigation Team (QASSIT) Acid Sulfate Soils Laboratory Methods Guidelines (Ahern et al. 2004).

A1.4.2 Field pH test (pH_F) – NSM-1.1

The procedure for the pH_F is outlined below:

- Calibrate battery powered field pH meter according to manufacturer’s instructions.
- Prepare the centrifuge tubes in a tube rack. Mark the rack with the depths to identify the top and bottom of the profile. Use separate racks for the pH_F and pH_{FOX} tests to prevent cross contamination from violent pH_{FOX} reactions.
- Conduct tests at intervals on the soil profile of 0.25 m, or at least one test per soil layer/horizon, whichever is lesser.
- For each layer place approximately half a teaspoon of soil into each of the pH_F and pH_{FOX} tubes. It is important the two sub-samples come from the same depth and are similar in characteristics. For example, do not take half a teaspoon of grey mud from the 0–0.25 m depth for one test and then select half a teaspoon from the same depth layer that has yellow mottles for the other test.

- Place enough deionised (DI) water in the pH_F test tube to make a paste similar to 'grout mix' or 'white sauce'; stir the soil:water paste to ensure all soil 'lumps' are removed (demineralised water can be substituted; never use tap water). Water must be added to the soil samples within 10 min of sampling to reduce the risk of RIS oxidation; monosulfidic material may start to oxidise in less than 5 min, substantially affecting pH_F results.
- Immediately place the pH spear point electrode into the soil:water paste, ensuring the spear point is completely submerged. Never stir the paste with the electrode as this may damage the semi-permeable glass membrane.
- Measure the pH_F with the calibrated pH meter.
- Wait for the reading to stabilise and record the pH measurement.
- All measurements should be recorded on a data sheet.

A1.4.3 Field pH peroxide test (pH_{FOX}) – NSM-1.2

It is recommended that 30% hydrogen peroxide (H_2O_2) be used in the pH_{FOX} test.

Hydrogen peroxide (30%) is highly corrosive and care should be taken when handling and using the peroxide. Safety glasses and gloves should be worn when handling and using peroxide. All chemical bottles should be clearly labelled and Safety Data Sheets (SDS) should be kept with the chemicals at all times. Appropriate health and safety precautions should be adhered to. Peroxide should be kept in the fridge when not in use.

The procedure for the field pH peroxide test (pH_{FOX}) is outlined below:

- Adjust the pH of the H_2O_2 to between 4.5 and 5.5 before going into the field. While stirring, add a few drops of dilute NaOH and regularly check the pH with a calibrated electrode until the correct range is reached. Allow the peroxide to stand for 15 min and then recheck the pH. As H_2O_2 degrades over time, only buffer small quantities at a time and refrigerate when not in use.
- Calibrate battery powered field pH meter according to manufacturer's instructions.
- Prepare heat-resistant centrifuge tubes in a tube rack. Mark the rack with the depths to identify the top and bottom of the profile. Use separate racks for the pH_F and pH_{FOX} tests to prevent cross contamination from violent pH_{FOX} reactions.
- Conduct pH_{FOX} tests at intervals on the soil profile of 0.25 m or at least one per horizon, whichever is lesser.
- To the pH_{FOX} tube, prepared while sampling for pH_F, add sufficient 30% H_2O_2 (at room temperature) to cover the soil, then stir the mixture.
- Rate the reaction of soil and peroxide using the reaction scale in Table A1.
- Allow approximately 15 min for any reactions to occur. The reaction may be rapid and vigorous if substantial RIS is present. If the reaction is violent and the soil:peroxide mix may overtop the tube, use a wash bottle to add small amounts of deionised or demineralised water to cool and calm the reaction. Do not add too much water as this may dilute the mixture and affect the pH value.
- Add a further 1–2 mL of H_2O_2, mix, allow to react for 15 min and rate the reaction. Continue this process until the soil:peroxide mixture reaction has slowed. This will ensure most of the RIS have reacted.
- If there is no initial reaction, individual tubes containing the soil:peroxide mixture can be placed in direct sunlight. This may encourage the initial reaction to occur.

- Wait for the soil:peroxide mixture to cool. This may take up to 10 min as the reaction can exceed 90 °C. Check the temperature rating of the pH meter and probe as high temperatures can damage the electrode and result in inaccurate readings. A more accurate pH is recorded if a temperature probe is used, however, this may be impractical in some field situations.
- Place the spear point pH electrode into the soil:peroxide mixture, ensuring the spear point is completely submerged. Never stir the paste with the electrode as this may damage the semi-permeable glass membrane.
- Measure the pH_{FOX} with the calibrated pH meter.
- Wait for the reading to stabilise and record the pH_{FOX} measurement.
- All measurements should be recorded on a data sheet.

Rating soil reactions of the pH_{FOX} test

Table A1 indicates the reaction scale for pH_{FOX} tests. The rate of the reaction generally indicates the level of RIS present, but depends also on texture and other soil constituents. A soil containing very little RIS may only have a slight reaction (L), however a soil containing high levels of RIS (remember the exact level of RIS cannot be determined using the pH_{FOX} test) is more likely to have an extreme/volcanic reaction (X–V), although there are exceptions. This rating scale alone should not be used to identify ASS. It is not a very reliable feature in isolation as there are other factors including manganese and organic acids which may trigger reactions. Reactions with organic matter tend to be more ‘frothing’ and do not tend to generate as much heat as sulfidic reactions. Manganese reactions can be quite extreme, but do not tend to lower the pH_{FOX}.

Table A1 Soil reaction rating scale for the pH_{FOX} test.

Reaction scale	Rate of reaction
L	Low reaction
M	Medium reaction
H	High reaction
X	Extreme reaction
V	Volcanic reaction

Source: DER (2015a).

A1.4.4 Interpretation of field pH tests

The pH_F test can help identify Actual ASS. While a pH_F of less than or equal to 4 is indicative of the presence of Actual ASS, it is not conclusive of the presence of ASS on its own, as naturally occurring, non ASS soils such as many organic soils (for example peats) and heavily leached soils may also have pH_F less than or equal to 4. To identify as an Actual ASS, other evidence must be presented that indicates that the low pH_F has been mainly caused by the oxidation of RIS. Such information includes the presence of jarosite in the soil layer/horizon, or the location of other Actual ASS or PASS materials within or in the nearby vicinity to the sampling location.

The difference between the pH_F and the pH_{FOX} is helpful in the preliminary identification of PASS. Combined the pH_F and pH_{FOX} results can be a useful aid with soil sample selection for laboratory analysis during Stage 2 of the field site investigations.

The pH_{FOX} result when compared to the pH_F result can give an indication of the presence of RIS in the sample. To ensure accurate results both of these tests must be conducted in the field as soon as possible after the sample is collected as the pH of the soil sample can change relatively quickly with time (hours to days) even when recommended sample preservation techniques are employed. For example, it is not unusual for soil pH test carried out at a laboratory to differ considerably (that is greater thana pH unit) from soil pH test measured in the field after even one day of storage, and as such, a laboratory determination of pH_F at a later date cannot be relied upon to represent field conditions at the time of sampling.

Soil field pH_F and pH_{FOX} tests whilst useful exploratory tools, however, are not determinative and cannot be substituted for laboratory analysis for either the identification of ASS materials and quantification of the acidity hazards these materials pose. A recent review of the utility of these field tests in Western Australia indicated that these tests only accurately identified ASS materials in 60 to 80 per cent of cases (DER 2015a).

A comparison of pH_F and pH_{FOX} test results can often give a strong indication of the presence of ASS. The greater the drop in pH from pH_F following the addition of peroxide, the greater the likelihood of PASS, although there are exceptions. A combination of a large difference between the two pH tests, a strong reaction with peroxide and a low pH after peroxide oxidation (that is pH_{FOX} less than 3) strongly indicates the presence of PASS.

However, it is important to note that the definitive confirmation of either the presence or absence of PASS materials in the field can only be accomplished by appropriate laboratory testing.

Tables A2 and A3 provide some guidance on the interpretation of pH_F and pH_{FOX} test results, respectively.

Table A2 Interpretation of some pH_F test ranges.

pH value	Result	Comments
$pH_F \leq 4$, jarosite not observed in the soil layer/horizon	May indicate an AASS indicating previous oxidation of RIS or may indicate naturally occurring, non ASS soils	Generally not conclusive as naturally occurring, non ASS soils, such as many organic soils (for example peats) and heavily leached soils, often also return $pH_F \leq 4$
$pH_F \leq 4$, jarosite observed in the soil layer/horizon	The soil material is an AASS	Jarosite and other iron precipitate minerals in ASS such as schwertmannite require a pH < 4 to form and indicate prior oxidation of RIS
$pH_F > 7$	Expected in waterlogged, unoxidised, or poorly drained soils	Marine muds commonly have a pH > 7 which reflects a seawater (pH 8.2) influence. Oxidation of samples with H_2O_2 can help indicate if the soil materials contain RIS

Source: Adapted from DER (2015a).

Table A3 Interpretation of pH_{FOX} test results.

pH value and reaction	Result	Comments
Strong reaction of soil with H_2O_2 (that is X or V)	Useful indicator of the presence of RIS but cannot be used alone	Organic rich substrates such as peat and coffee rock, and soil constituents like manganese oxides, can also cause a reaction. Care must be exercised in interpreting these results. Laboratory analyses are required to confirm if appreciable RIS is present

pH value and reaction	Result	Comments
pH_{FOX} value at least one unit below field pH_F and strong reaction with H_2O_2 (that is X or V)	May indicate PASS	The difference between pH_F and pH_{FOX} is termed the ΔpH. Generally the larger the ΔpH the more indicative of PASS. The lower the final pH_{FOX} the better the likelihood of an appreciable RIS content. For example, a change from pH_F of 8 to pH_{FOX} of 7 (that is a ΔpH of 1) would not indicate PASS, however, a unit change from pH_F of 3.5 to pH_{FOX} of 2.5 would be indicative of PASS. Laboratory analyses are required to confirm if appreciable RIS is present
$pH_{FOX} < 3$, large ΔpH and a strong reaction with H_2O_2 (that is X or V)	Strongly indicates PASS	The lower the pH_{FOX} below 3, the greater the likelihood that appreciable RIS is present. A combination of all three parameters – pH_{FOX}, ΔpH and reaction strength – gives the best indication of PASS. Laboratory analyses are required to confirm that appreciable RIS is present
A pH_{FOX} 3–4 and Low, Medium or Strong reaction with H_2O_2	Inconclusive	RIS may be present; however, organic matter may also be responsible for the decrease in pH. Laboratory analyses are required to confirm the presence of RIS
pH_{FOX} 4–5	Inconclusive	RIS may be present in small quantities, or poorly reactive under rapid oxidation, or the sample may contain shell/ carbonate which neutralises some or all acid produced on oxidation. Equally, the pH_{FOX} value may be due to the production of organic acids with no RIS present. Laboratory analyses are required to confirm if appreciable RIS is present
$pH_{FOX} > 5$, small or no ΔpH, but Low, Medium or Strong reaction with H_2O_2	Inconclusive	For neutral to alkaline pHF with shell or white concretions, the fizz test with 1 M HCl can be used to identify the presence of carbonates. Laboratory analyses are required to confirm if appreciable RIS is present and further testing is required to confirm that effective self-neutralising materials are present

Source: Adapted from DER (2015a).

A1.5 Field carbonate test – NSM-2.1

The field carbonate test (commonly referred to as the ‘fizz test’) is used to determine the presence of carbonates in soil. It is a quick, easy, cheap test to conduct in the field. The test should be conducted on samples suspected of containing carbonates (for example fine shell, crushed coral, et cetera). The carbonate content of the soil can be quantified in the laboratory by the determination of the Total Organic Carbon content (NLM-5.1) (Sullivan et al. 2017b). The field carbonate test outlined below is from the QASSIT Acid Sulfate Soils Laboratory Methods Guidelines (Ahern et al. 2004).

- Place approximately one teaspoon of soil into a clean, clear test tube. It is important that test tubes used in the fizz test are not used for the field pH tests as cross-contamination may occur, affecting pH readings.
- Place two or three drops of 1 M hydrochloric acid (HCl) onto the soil sample. HCl is highly corrosive so safety precautions must be exercised.
- Rate the reaction (see Table A4).
- All measurements should be recorded on a data sheet.

Table A4 Soil reaction rating scale for the fizz test.

Reaction scale	Rate of reaction
N – non-calcareous	No audible or visible effervescence
S – slightly calcareous	Slightly audible but no visible effervescence
M – moderately calcareous	Audible and slightly visible effervescence
H – highly calcareous	Moderate visible effervescence
V – very highly calcareous	Strong visible effervescence

Source: McDonald et al. (1990).